TABLE III. Experimental data and derived parameters.

| $a$ $(10^{-8}$ cm$)$ | $ac_{11}$ | $ac_{12}$ | $ac_{44}$ $(10^4$ dyne/cm$)$ | $\alpha$ | $\beta$ | $\mu$ | $M^{-1}$ $(10^{22}$ g$^{-1})$ |
|---|---|---|---|---|---|---|---|
| Si | 5.4307 | 8.991 | 3.467 | 4.317 | 8.423 | 5.235 | 0.071$_0$ | 2.1446 |
| Ge | 5.6575 | 7.295 | 2.735 | 3.799 | 7.221 | 4.869 | 0.010$_4$ | 0.8293$_7$ |

leading to Figs. 21, 22, and 23, while the same values of $\alpha$ and $\beta$ were used as before. Since $\mu$ is much smaller than $\alpha$ or $\beta$ (according to our model), this influences the results only slightly.

By comparing the experimental results of Macfarlane et al.[5,6] for $\theta_{LA}$ and $\theta_{TA}$ for pure silicon and germanium [see Table I] with those given by our calculations [see Fig. 18], it may be seen that there is a serious disagreement between these two sets of results. We have attempted to remedy this situation by constructing a number of five-parameter force models involving the two first-neighbor parameters $\alpha$ and $\beta$, and three independent second and/or third neighbor parameters. In each case, the five parameters were evaluated by fitting the theory to the experimental values of $c_{11}$, $c_{12}$, $c_{44}$, $\theta_{LA}$, and $\theta_{TA}$. Unfortunately, these models predict Raman frequencies which are unreasonably low. Since we have been unable to find a force system which fits all the available experimental information, and which at the same time appears physically realistic, we are reporting only the results for the original three-parameter force model.

Since the difference in the atomic masses for silicon and germanium accounts almost entirely for the difference in their lattice spectra, the choice of a force model is not as critical a matter as it would be otherwise. Even if we had assumed the same force system for silicon and germanium, the qualitative features of Figs. 18, 21, 22, and 23 would remain essentially the same. However, it is rather disturbing that we were unable to find a satisfactory force model within the framework of the Born-Smith theory.

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# Electrical Conductivity of X-Irradiated NaCl

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The electrical resistance of Harshaw sodium chloride crystals exposed at room temperature to x-ray doses sufficient to produce about $6\times10^{16}$ $F$ centers/cm$^3$ has been measured as a function of time at constant temperatures between 150 and 200°C. The effects of previous heat treatment of the crystals, x-ray dose, temperature of measurement, and preliminary optical bleaching have been observed. Initially the resistance of irradiated crystals is much greater than that of unirradiated ones. The resistance of the colored crystals at first decreases rapidly (for about 10 to 100 minutes, depending on the temperature). In the case of crystals used as received from Harshaw, the resistance even falls slightly below that of the normal uncolored crystals. Subsequently the resistance again increases, reaching a constant value (after about 50 to 1000 minutes) higher than for the normal crystal. If the crystals are optically bleached before the measurement, the resistance increase recovers very much more slowly. The behavior can be restored to normal by annealing above 250°C. The slow resistance increase is seen as evidence for the production by the x-rays of excess positive-ion vacancies.

## I. INTRODUCTION

LARGE increases of electrical resistivity have been observed in sodium chloride and other alkali halide crystals which have been subjected to ionizing radiation, whether gamma rays,[1] x-rays,[2] or protons.[3,4] These radiations also produce color centers in the crystals,[5] so that such changes should be expected if formation of some of the color centers involves neutralization or immobilization of charge carriers. Since these crystals are ionic conductors in which only positive ion vacancies are mobile at low temperatures,[6] the capture of a positive hole formed by the radiation at a positive-ion vacancy in the lattice, i.e., according to Seitz's model[5] the formation of a $V_1$ center, would be such an event. (The $V_1$ centers actually are unstable at room temperature, but other more complicated possibilities exist.)

On the other hand, since the number of color centers deduced from the intensity of coloration is greater than the number of vacancies thought to be normally present in the lattice, it is believed that the ionizing radiation is also capable of producing extra vacancies. In fact, density changes accompanying irradiation have

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[1] Nelson, Sproull, and Caswell, Phys. Rev. 90, 364 (1953).
[2] F. A. Cunnell and E. E. Schneider, Phys. Rev. 95, 598 (1954).
[3] E. A. Pearlstein, Phys. Rev. 92, 881 (1953).
[4] K. Kobayashi, Phys. Rev. 102, 348 (1956).
[5] For a review, see F. Seitz [Revs. Modern Phys. 26, 7 (1954)].

[6] Tubandt, Reinhold, and Leibold, Z. anorg. u. allgem. Chem. 197, 225 (1931).

been regarded as confirmation of this production.[7-9] This process would lead to a decrease of resistivity unless the extra vacancies were neutralized. No indication of extra vacancy production has been seen in previous resistance measurements.

Electrical resistivity measurements, which furnish information about the number of mobile charged lattice defects, made under various conditions of coloration and correlated with optical absorption measurements, can provide evidence about the structure of the various color centers. We have measured the resistance of sodium chloride crystals as a function of time at a constant elevated temperature, after the crystals have been irradiated with x-rays at room temperature. The observations of the resulting isothermal processes are easier to interpret than are the warmup curves previously published. The measurements have been made under different conditions of previous heat treatment, amount of irradiation, and temperature of measurement, and for crystals which were colored and then optically bleached before the measurement.

## II. EXPERIMENTAL DETAILS

### 1. Preparation of Samples

All samples used in this investigation were cleaved from one sodium chloride single crystal obtained from the Harshaw Chemical Company. After cleaving they were subjected to one of the following treatments: (i) No further heat treatment was given, a condition which will be called "as received." (ii) An eight-hour anneal in air at 600°C was followed by slow cooling over six days to 265°C and a four-day anneal at that temperature. These will be referred to as "slowly cooled" crystals. (iii) After a two-hour anneal at 660°C, the samples were furnace-cooled to room temperature, with a maximum cooling rate of 20°/min. These will be called "rapidly cooled."

The size of the samples was about $0.9 \times 0.7 \times 0.1$ cm. After heat treatment, graphite electrodes were applied to the two large faces by painting on colloidal graphite (Aquadag) in ethyl alcohol. The edges were then polished on a wet paper towel.

### 2. X-Ray Irradiation and Optical Bleaching

The samples were colored by radiation from a Norelco skin-therapy x-ray unit with a tungsten target, operated at 50 kvp and 2 ma. This machine has an inherent filtration equivalent to that of 0.3-mm aluminum, and produces 9000 roentgens per minute about 2 cm from the target where the samples were placed. For all the data reported here a KCl or NaCl filter about 0.7 mm thick was put in front of the sample, but this filtration did not make much difference in the results. A 10-minute irradiation produced about $6 \times 10^{16}$ F centers/

cm³, corresponding by Smakula's formula[10] to the measured absorption coefficient of 8.9 cm⁻¹ at the F-band maximum.

Some of the specimens were optically bleached with white light before the resistance measurement. For this purpose they were placed 10 cm from a 100-w tungsten filament lamp bulb. Some were exposed instead to light which also contained an ultraviolet component, namely a Spindler and Hoyer 5-amp carbon arc placed 20 cm away. The illumination was from the edge, because the opaque electrodes were intact. Samples which were not to be bleached were exposed to dim light for about 15 seconds in transferring them from the box in which they were irradiated to the measuring apparatus.

### 3. Resistance Measurement

The electrical resistance of the crystals was measured with a General Radio Company electrometer-amplifier Type 1230-A, which can measure a maximum resistance of $10^{14}$ ohms. This is a dc measurement, but the charge passed through the crystal for one reading was at most about $2 \times 10^{-9}$ coulomb, and usually much less.

The resistance measurements were made at elevated temperatures with the sample sandwiched between spring-loaded silver electrodes in a furnace whose temperature was controlled to $\pm 0.5°$ by a proportioning temperature controller.[11] A chromel-alumel thermocouple was soldered to one silver electrode. The measurement was nearly isothermal, since three minutes after the specimen was put into the preheated furnace the specimen temperature was within about 3° of the furnace temperature. At one minute its temperature was about 15° lower. The measured resistance was corrected to that at the nominal temperature of the run by using the measured temperature dependence of the resistance of unirradiated samples.

### III. RESULTS

The resistance of x-ray irradiated crystals was measured as a function of time of annealing at constant temperature, for various heat treatments, times of irradiation, and annealing temperatures, and for optically bleached crystals. The general effect of the radiation was a large increase of resistivity (Fig. 1), in agreement with the results of Kobayashi.[4] The data will be presented as a ratio of the conductivity $\sigma$ of the irradiated crystal to the conductivity $\sigma_0$ of the same crystal measured before the irradiation ("normal crystal"). The conductivity $\sigma_0$ of most of the normal crystals used was given by $\sigma_0 = (2.9 \times 10^5/T) \exp(-28\,800/RT)$ (ohm-cm)⁻¹ between 150° and 200°C. More than one run was made on each crystal. After a run the conductivity was restored to the normal value by annealing

[7] Estermann, Leivo, and Stern, Phys. Rev. **75**, 627 (1949).
[8] L. Y. Lin, Phys. Rev. **102**, 968 (1956).
[9] K. Kobayashi, Phys. Rev. **107**, 41 (1957).

[10] A. Smakula, Z. Physik **59**, 603 (1930).
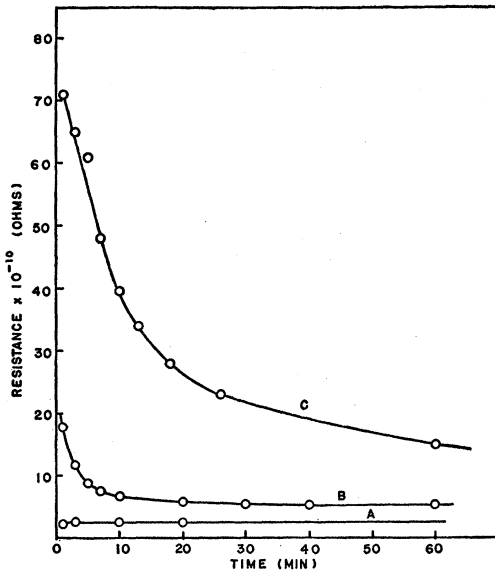[11] R. W. Christy, J. Sci. Instr. **33**, 365 (1956).

FIG. 1. Resistance of rapidly cooled NaCl crystals as a function of time at 173°C. (A) Unirradiated. (B) Irradiated 10 minutes. (C) Irradiated 10 minutes and bleached with white light.

for three hours at 263°C. After many irradiations of one crystal there was a gradual irreversible increase of resistance, but the conductivity of all samples was within about 30% of the above value.

## 1. Effect of Heat Treatment

The relative conductivity measured as a function of time at 173°C, after a 10-minute x-ray irradiation at
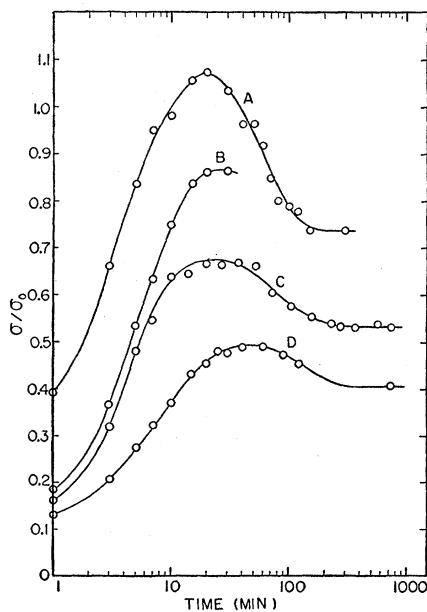


FIG. 2. Effect of heat treatment on relative conductivity at 173°C of NaCl irradiated 10 minutes. (A) As received from Harshaw. (B) Same crystal, irradiated again after annealing. (C) Slowly cooled. (D) Rapidly cooled.

room temperature, is shown in Fig. 2 for crystals with different histories. Curve A is for a virgin sample cleaved from the large NaCl crystal as received from Harshaw. Curve B is for the same crystal, irradiated a second time after recovery of the normal conductivity at 263°C. Curves C and D are, respectively, for samples slowly cooled from 600° and rapidly cooled from 660°C.

In each case the conductivity was initially less than the normal value and increased rapidly with time. Later it reached a maximum value and subsequently decreased slowly to an asymptotic value less than the normal conductivity but greater than the initial value. This general behavior was characteristic of all colored specimens observed. The only specimens, however, which at any time attained a conductivity greater than normal were the virgin ones. The slowly cooled specimens behaved more nearly like the as-received crystals than did the rapidly cooled ones, in agreement with
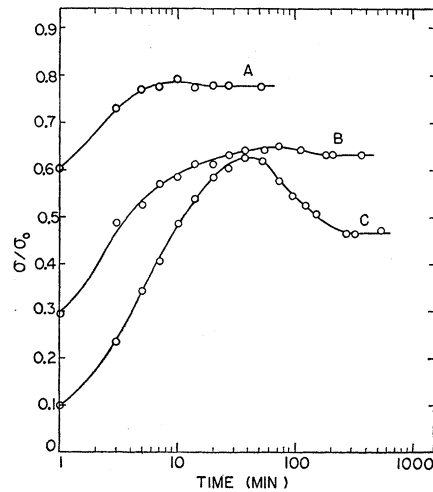


FIG. 3. Effect of x-ray dose on relative conductivity at 173°C of slowly cooled NaCl. (A) 0.1-min irradiation. (B) 0.5-min. (C) 10-min.

evidence from the darkenability[12] that crystals as received from Harshaw are in a very well annealed state.

## 2. Effect of Time of Irradiation

The behavior of a slowly cooled crystal measured at 173°C after irradiations of 0.1 min (curve A), 0.5 min (curve B), and 10 min (curve C) is shown in Fig. 3. Even with a 0.1-min irradiation the initial and final decrease of conductivity was appreciable, the effect on the conductivity increasing rather slowly with duration of irradiation. The notable feature of the 10-min irradiation compared with the smaller doses was the pronounced conductivity maximum which it produced.

## 3. Temperature Dependence

Figure 4 shows the relative conductivity of a rapidly cooled crystal irradiated for 10 min, measured at 151°,

[12] R. B. Gordon and A. S. Nowick, Phys. Rev. 101, 977 (1956).

173°, 188°, and 203°C. At higher temperature the initial rate of increase of conductivity was larger, the maximum and final values were reached earlier, and the final value was higher. A slowly cooled crystal measured at the same temperatures showed the same general behavior, though the initial rate of change was greater, the maxima were more pronounced, and some of the curves crossed each other.

The shape of the curves suggests that two processes are involved in the recovery of the conductivity, the one leading to a rapid increase and the other to a slow decrease. As a measure of the rate of the first of these processes the initial slope of the curves was used. This is described by the formula $1.4 \times 10^5 \exp(-17\,000/RT)$ $\sec^{-1}$ for the data of Fig. 4, with an estimated uncertainty of about 2 kcal/mole in the activation energy. For the slowly cooled sample the rate was about three times greater but with the same activation energy.
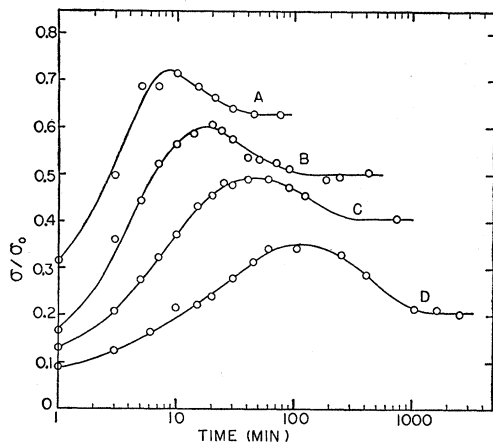


FIG. 4. Effect of temperature on relative conductivity of rapidly cooled NaCl irradiated 10 min. (A) 203°C. (B) 188°C. (C) 173°C. (D) 151°C.

For the time constant of the slow process the time required to reach the final value of conductivity was used. This is described for both crystals by $3.8 \times 10^8 \times \exp(-26\,300/RT)$ $\sec^{-1}$, with an uncertainty of about 2 kcal/mole.

The measured initial slope is probably an underestimate of the true isothermal decay rate, since the temperature of the sample was lower during the first two or three minutes in the furnace. The activation energy, however, probably is not far off.

### 4. Effect of Optical Bleaching

Samples which were x-ray colored for 10 min and then optically bleached had a much greater resistance than those which were x-ray colored but not bleached. Curve B of Fig. 5 shows the relative conductivity at 173°C of a rapidly cooled sample which was bleached with white light before the measurement, compared to a
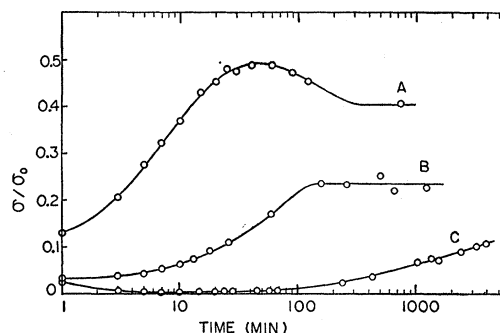


FIG. 5. Effect of optical bleaching on relative conductivity at 173°C of NaCl x-irradiated 10 min. (A) Rapidly cooled, colored. (B) Rapidly cooled, bleached with white light. (C) Slowly cooled, bleached with white light.

colored sample (curve A). The recovery is very much slower and less complete in the case of the bleached sample. The effect of bleaching is even more striking in the case of a slowly cooled sample (curve C), where the initial change of the conductivity was an even further decrease.

The F band was much more stable against optical bleaching in the slowly cooled crystal than in the rapidly cooled one. In both cases the bleaching was continued until the crystal appeared colorless. This state was reached in 10 minutes with the rapidly cooled sample, but required 45 minutes for the slowly cooled one.

Bleaching with a source containing ultraviolet in addition to visible light led to a behavior which was similar, though the decay of resistance was somewhat more rapid.

### IV. DISCUSSION

In interpreting the changes of conductivity occurring in the irradiated crystals at constant temperature, it will be assumed in the following discussion that the current is carried by $n$ singly charged defects, all with the same mobility $\mu$, so that the conductivity is $\sigma = ne\mu$. This assumption may not be rigorously true if charged vacancy complexes give a contribution to the current in addition to single positive-ion vacancies; Dienes[13] has calculated, for example, that an anion-cation pair of vacancies has a jump frequency with an activation energy somewhat lower than that of a single vacancy. As a simplifying assumption it should give a qualitatively correct picture, however. Secondly it will be assumed that the number of charge carriers in the normal crystal is constant, in particular independent of temperature in the range between 150 and 200°C. This assumption also may be only an approximation, but if it is made the relative conductivity curves can be taken to represent the instantaneous number of charge carriers, relative to the number in the normal crystal.

[13] G. J. Dienes, J. Chem. Phys. 16, 620 (1948).

The conductivity of all irradiated crystals was found to be less than that of the normal crystals, so that the primary effect of the radiation is to neutralize or immobilize charge carriers, including the majority of any extra positive-ion vacancies that are produced by the radiation. The formation of both $V_3$ and $V_2$ centers would have this effect, according to Seitz's model,[5] since they consist of pairs of cation vacancies which have captured one or two positive holes. At least 90% of the vacancies appear to be neutralized.

In all of the colored crystals, furthermore, there is initially a rapid increase of conductivity at elevated temperatures, and an approach to a constant or nearly constant value after a long time, which asymptotic value is greater the higher the temperature but always less than the normal value. This behavior is qualitatively similar to an inverted thermal bleaching curve,[14–16] as should be expected if the number of color centers is equal to the deficit of charge carriers. An activation energy of about 0.75 ev was found for the initial rate of decrease of resistance. It is possible that a similar value would be found for the thermal bleaching of $V_2$ centers (although for thermal bleaching of $F$ centers a much smaller value of activation energy has been reported[15]).

The maximum in the conductivity curves suggests that there is another effect, which tends to increase the number of charge carriers and which anneals more slowly than the bleaching of the color centers. This may be the production of extra positive-ion vacancies by the radiation. Their number would return to normal at a rate determined by their mobility. The activation energy of 26 kcal/mole observed for this slower process is somewhat greater than the value of 20 kcal/mole for the mobility of positive-ion vacancies derived from conductivity measurements.[17] In order to preserve charge neutrality, however, the extra positive-ion vacancies would have to disappear at the same rate as the excess negative-ion vacancies. The observed activation energy, on the other hand, is much smaller than the value of 39 kcal/mole which can be deduced for the single negative-ion vacancies from the diffusion coefficient[18] of Cl⁻ and the number of vacancies,[17] consistently with the transfer numbers.[6] Possibly at these low temperatures the positive and negative vacancies diffuse away as anion-cation vacancy pairs, with an activation energy of 26 kcal/mole.

If one accepts this interpretation, the number of vacancy sinks $N$ can be estimated from the observed pre-exponential factor $\lambda_0$ in the rate of the slow con-

ductivity decrease. The decay constant for the excess vacancies is $Nv\sigma$, where $v$ is their drift velocity and $\sigma$ the capture cross section. Letting $v = a\nu \exp(-26\,300/RT)$ and $\sigma = \pi a^2$, with $a$ of the order of the lattice distance, we have

$$N = \lambda_0/\pi a^3 \nu.$$

Taking $\nu = 10^{13}$ sec⁻¹ and $a = 4\times 10^{-8}$ cm, with the observed value $\lambda_0 \cong 6\times 10^8$ sec⁻¹, we get $N \cong 10^{17}$ cm⁻³. If the vacancies can disappear at any point along a dislocation line, this number corresponds to about $10^{10}$ dislocation lines/cm², a reasonable number.

Our exponential temperature dependences of the foregoing processes can be compared with warmup curves if it is assumed that the time dependence is exponential, so that the rate of change of the number $n$ of objects of interest is given by $dn/dt = -\lambda n$, with $\lambda = \lambda_0 \exp(-H/RT)$. During a warmup in which the temperature $T$ changes at a constant rate, $dT/dt = \alpha$, the number $n$ can be approximately integrated in case $H/RT \gg 1$:

$$n(T) = n_0 \exp\{-RT^2\lambda(T)/\alpha H\}.$$

The number is half the initial number $n_0$ when

$$T = H/R \ln(RT^2\lambda_0/\alpha H \ln 2).$$

Upon using our data for the initial fast rise of the conductivity, the half-value temperature is 160–180°C for a temperature rise of 2°/min. This temperature can be correlated with the peak of resistance near 150°C observed by Kobayashi.[4] For the second slow process we obtain the temperature 215°C for the half-value, in good agreement with Kobayashi's data[9] for the recovery during warmup of the volume increase produced by irradiation.

If the above mechanisms are the correct explanation of the conductivity changes, it would appear that the 10-minute irradiation produces an excess of positive-ion vacancies equal to about one-tenth to one-third of the number already present in the normal crystal. All or most of these are initially neutralized by positive holes. The number produced in the crystals as received from Harshaw is greater than that in a carefully annealed crystal or one that was rapidly cooled after annealing at 660° (not only the relative number but also the absolute number, since the normal conductivity was the same). In the crystals as received, irreversible changes take place as a result of irradiation, probably because neutral vacancy clusters remain in the crystal[9] after annealing at 263°C, and the behavior approaches that of the annealed samples.

The effect of irradiation does not increase proportionally to the amount of irradiation. The production of vacancies, however, is a relatively more pronounced effect of longer irradiation than the neutralization of the charge carriers. That is, small doses produce relatively enormous conductivity decreases, compared to larger doses, but the production of vacancies is more

[14] Casler, Pringsheim, and Yuster, J. Chem. Phys. **18**, 887 (1950).

[15] E. E. Schneider, *Fundamental Mechanisms of Photographic Sensitivity* (Butterworths Scientific Publications, London, 1951), p. 13.

[16] Mador, Wallis, Williams, and Herman, Phys. Rev. **96**, 617 (1954).

[17] H. W. Etzel and R. J. Maurer, J. Chem. Phys. **18**, 1003 (1950).

[18] M. Chemla, Compt. rend. **234**, 2601 (1952).

nearly proportional to the dose. This difference is reasonable, if the vacancies present in the normal crystal first trap electrons and holes.

The difference between colored and optically bleached crystals is striking. When irradiated crystals are illuminated with light absorbed by the $F$ centers, in addition to the bleaching of the $F$ band and the formation of $R$ and $M$ centers, the $V_2$ centers are bleached (probably being converted to $V_3$ centers); the $V_3$ band is stable.[14] This behavior is understandable in terms of Seitz's model: some of the electrons optically released from the $F$ centers annihilate positive holes in $V_2$ centers (converting them to $V_3$); $V_3$ centers repel electrons electrostatically because they are charged and thus resist bleaching.[5] The $V_3$ centers are also more stable thermally than the $V_2$. Now when a neutral $V_2$ center is converted into a charged $V_3$ by capture of an electron optically released from an $F$ center, the number of charge carriers is increased, in contrast to the observations on bleached samples, unless the $V_3$ centers are immobile. Thus this model leads to the conclusion that the $V_3$ centers cannot move. This being so, it further entails the assumption that $V_2$ centers are converted to other than the stable $V_3$ centers by thermal bleaching, since the conductivity of colored crystals rapidly increases.

A fundamental assumption of the foregoing discussion is that the contribution to the current from $F$-center electrons thermally excited to the conduction band is negligible. An excess conductivity in electrolytically colored crystals at high temperature, with an activation energy of about 1 ev, has been attributed to such conduction electrons.[19] This excess, extrapolated to the temperature of our experiment, gives a value comparable with our observed values. Because the $F$-center dissociation reaction involves vacancies present in thermal equilibrium number, however, the thermal activation energy for excitation of an $F$-center electron to the conduction band deduced[20] from these data is close to 2 ev. At lower temperatures where the number of vacancies is constant, the electronic component of conductivity would vary with the higher activation energy and would be negligible in our temperature range. On the other hand, if the thermal activation energy of the $F$-center electron were actually close to 1 ev, as is not unlikely on theoretical grounds,[21] then our slowly annealing excess conductivity might be attributable to electrons instead of to excess vacancies produced by the radiation. In this case trapping of $F$-center electrons at (thermally) deeper $R$- and $M$-center traps would tend to reduce the conductivity of the optically bleached crystals.

## V. ACKNOWLEDGMENTS

[19] A. Smakula, Göttingen Nachrichten 1, 55 (1934).
[20] N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Oxford University Press, Oxford, 1948), second edition, p. 143.
[21] N. F. Mott and R. W. Gurney, reference 20, p. 162.